

# FERTILIZER METHODS

Chapter

PHOSPHATE ANALYSIS

Subject

Citrate Insoluble Phosphorus – Flow Injection

**SCOPE:** This is a double extraction, automated analytical procedure for the determination of citrate insoluble phosphorus in fertilizer samples that have a range of 0 to 20%  $P_2O_5$ , the range may be increased by decreasing sample weight and/or the use of dilutions.

**PRINCIPLE:** The preparation for citrate insoluble phosphorus is achieved by extracting the phosphate from the fertilizer sample with D.I. water at 65° C and neutral ammonium citrate solution at 65° C. The sample residue is then ignited and digested with hydrochloric acid. The automated colorimetric determination of phosphorus in fertilizer samples is achieved by using a heated manifold (95° C) and perchloric acid to destroy ammonium citrate, to destroy other colored materials, and to hydrolyze available phosphate to orthophosphate. The orthophosphate/molybdovanadate color complex is read at 420 nm.

**SAFETY:** Each laboratory is responsible for maintaining a current file of the Occupational Health and Safety Act (OSHA) regulations regarding the safe handling of the chemicals specified in this method. A reference file of Material Safety Data Sheets (MSDS) should be made available to all personnel involved in the chemical analysis.

## APPARATUS & EQUIPMENT:

- Balance, accuracy to 0.0001 g
- Circulating Water Bath, (65°C)
- Beaker, 250 mL Conical
- Filter Paper, 7 cm Whatman No. 1 or equivalent
- Filter Paper, 7 cm Whatman No. 5 or equivalent
- Flask, 500 mL Kohlrausch (class “A”)
- Funnel, Buchner 7 cm
- 30 Liter Glass Vessel
- Heater, for Ammonium Citrate Solution

- # 9 Stopper, Two Hole, for 500 mL Kohlrausch Flask
- #61/2 Stopper, One Hole, for 250 mL Conical Beaker
- Thistle Tube, Polyethylene
- Muffle Furnace or equivalent
- Flow Injection Analyzer
- Automatic Sampler
- Peristaltic Pump
- Pump tubes
- Manifold tubing
- Class “A” Amber Volumetric Flask
- Class “A” Pipets
- Filter Columns, disposable 40-50microns
- Culture Tubes, disposable borosilicate glass 13 x 100 mm or equivalent
- Helium with a degassing tube
- Handheld mixer

**REAGENTS &  
CHEMICALS:**

- Citric Acid Monohydrate [ $C_6H_8O_7 \cdot H_2O$ ] Certified A.C.S. grade or equivalent
- Ammonium Hydroxide [ $NH_4OH$ ] Certified A.C.S. grade or equivalent
- Ammonium Molybdate (VI) tetrahydrate [ $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ ] Certified A.C.S. grade or equivalent
- Ammonium Meta-Vanadate [ $(NH_4)VO_3$ ] Certified A.C.S. grade or equivalent
- Deionized (D.I.) water
- Nitric Acid [ $HNO_3$ ] Certified A.C.S. grade or equivalent
- Perchloric Acid [ $HClO_4$ ] Certified A.C.S. grade or equivalent
- Sulfuric Acid [ $H_2SO_4$ ] Certified A.C.S. grade or equivalent
- Hydrochloric Acid [ $HCl$ ] Certified A.C.S. grade or equivalent
- Potassium Phosphate Monobasic [ $KH_2PO_4$ ], Primary Standard Certified
- Ammonium Phosphate Dibasic [ $(NH_4)_2HPO_4$ ], Certified A.C.S. grade or equivalent
- Ammonium Citrate Solution

Citrate Acid Monohydrate	370 g
D.I. water	2 L

Ammonium Hydroxide 345 mL

In a 2L volumetric flask containing 1500 mL of D.I. water dissolve 370g of citric acid. With stirring add 345 mL of 28-30%  $\text{NH}_4\text{OH}$  mL to the flask. Allow solution to cool. Adjust pH to 7.00 by adding small increments of 1:1 ammonium hydroxide. Dilute to 2L with D.I. water. Mix thoroughly.

- 20% (v/v) Ammonium Citrate Solution

Ammonium Citrate Solution 400 mL

D.I. water 2 L

To a 2 Liter volumetric flask add approximately 1400mL of D.I. Water. To the flask add 400mL of ammonium citrate solution. Bring to volume and mix thoroughly.

- Molybdate Reagent

Ammonium Molybdate (VI) tetrahydrate  $[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}]$  40 g

D.I. water 2 L

Dissolve 40 g of ammonium molybdate in 1200 mL of D.I. water.

Adjust to pH 7.0 with 1:1  $\text{NH}_4\text{OH}$

Bring to volume and mix thoroughly.

- Vanadate Reagent

Ammonium MetaVanadate  $[(\text{NH}_4)\text{VO}_3]$  0.300 g

Sulfuric Acid  $[\text{H}_2\text{SO}_4]$  70 mL

D.I. water 2 L

To a 2 Liter volumetric containing 800 mL of D.I. water, add 70 mL of concentrated sulfuric acid. Add 0.300 g of ammonium metavanadate. Allow to cool, bring to volume, and mix thoroughly.

- 4 N Perchloric Acid, Digestion Reagent

70% Perchloric Acid 684 mL

D.I. water 2 L

To a 2 Liter volumetric containing 800 mL of D.I. water, add 684 mL perchloric acid. Bring to volume and mix thoroughly.

- 2.5 N Perchloric Acid, Carrier Reagent

70% Perchloric Acid 428 mL

D.I. water 2 L

To a 2 Liter volumetric containing 1200 mL of D.I. water, add 428 mL of perchloric acid. Bring to volume and mix thoroughly.

- 1:1 Ammonium Hydroxide

28 – 30% Ammonium Hydroxide 50 mL

D.I. water 100 mL

To a 100 mL volumetric containing 40 mL of D.I. water, add 50 mL of 28 – 30%

ammonium hydroxide. Bring to volume and mix thoroughly.

**NOTE: Reagents need to be degassed with Helium.**

### STANDARDS:

- $\text{KH}_2\text{PO}_4$  Stock Standard 2,500 ppm  $\text{P}_2\text{O}_5$   
 Monobasic Potassium Phosphate Primary Std. 2.3983 g  
 Ammonium Citrate Solution 100 mL  
 D.I. water 500 mL

Dissolve 2.3983 g of potassium monobasic phosphate primary standard (dried for 2 hours at 106°C) into a 500 mL volumetric flask containing 100 mL of ammonium citrate solution and 300 mL of D.I. water. Bring to 500 mL with D.I. Water. Mix thoroughly.

**Note: Working standards are diluted with 20% (v/v) Ammonium Citrate Solution.**

- Working Standard A 400 ppm  
 Pipet 40 mL of  $\text{KH}_2\text{PO}_4$  stock standard and dilute with 20% ammonium citrate solution to 250 mL. Mix thoroughly.
- Working Standard B 200 ppm  
 Pipet 20 mL of  $\text{KH}_2\text{PO}_4$  stock standard and dilute with 20% ammonium citrate solution to 250 mL. Mix thoroughly.
- Working Standard C 100 ppm  
 Pipet 10 mL of  $\text{KH}_2\text{PO}_4$  stock standard and dilute with 20% ammonium citrate solution to 250 mL. Mix thoroughly.
- Working Standard D 50 ppm  
 Pipet 5 mL of  $\text{KH}_2\text{PO}_4$  stock standard and dilute with 20% ammonium citrate solution to 250 mL. Mix thoroughly.
- Working Standard E 20 ppm  
 Pipet 2 mL of  $\text{KH}_2\text{PO}_4$  stock standard and dilute with 20% ammonium citrate solution to 250 mL. Mix thoroughly.
- Working Standard F 0 ppm  
 20% ammonium citrate solution

### SAMPLE PREPARATION:

1. Weigh sample directly into 250 mL conical beaker.

### NOTE ON WEIGHING SAMPLE:

- For 0-5% Guarantees, weigh  $\approx 3.00 \text{ g} \pm 0.10 \text{ g}$   
For 5-10% Guarantees, weigh  $\approx 2.00 \text{ g} \pm 0.10 \text{ g}$   
For 10-20% Guarantees, weigh  $\approx 1.00 \text{ g} \pm 0.10 \text{ g}$   
For 20-40% Guarantees, weigh  $\approx 0.5 \text{ g} \pm 0.10 \text{ g}$   
For Guarantees  $\geq 40\%$ , weigh  $\approx 0.25 \text{ g} \pm 0.10 \text{ g}$ , + a 1:2 dilution
2. Add 100 mL of D.I. water at 65° C to 250 mL conical beaker containing sample, seal with 1 hole stopper containing a thistle tube. Place in shaker bath at 65° C for 15 minutes.
  3. Set up Whatman No. 1 filter paper - Buchner funnel – Kohlrausch flask – vacuum apparatus.
  4. After 15 minutes remove conical beaker from shaker bath, wash thistle tube and stopper with D.I. water, at 65° C.
  5. Transfer contents of conical beaker to wetted Whatman No. 1 filter paper in Buchner funnel – Kohlrausch flask – vacuum apparatus. Rinse conical beaker and Buchner funnel with 100 mLs of D.I. water at 65° C in 10 mL increments. Allow each portion of the water to pass through the filter paper before adding the next portion. Vacuum dry filter paper.
  6. Carefully remove filter paper and place in conical beaker.
  7. Add 100 mL of ammonium citrate solution at 65° C to conical beaker, trying to place solution directly on the filter paper.
  8. Stopper with 1 hole stopper containing a thistle tube. Place in 65° C shaker bath for 1 hour.
  9. Add a Whatman No. 5 filter paper to Buchner funnel – Kohlrausch flask – vacuum apparatus.
  10. After one hour remove conical beaker from shaker bath, rinse thistle tube and stopper with D.I. water at 65° C.
  11. Transfer contents of conical beaker to wetted Whatman No. 5 filter paper in Buchner funnel – Kohlrausch flask – vacuum apparatus. Rinse conical beaker and Buchner funnel with 100 mL of D.I. water at 65° C in 10 mL increments. Allow each portion of the water to pass through the filter paper before adding the next portion. Vacuum dry filter paper.
  12. Remove filter paper and transfer it to a porcelain crucible.
  13. Ignite filter paper at 600° C until all organic matter has been destroyed.
  14. Cool crucible and contents.
  15. Transfer contents to 250 mL conical beaker and digest with 15 mL of HCl until all phosphate dissolves.
  16. Dilute to appropriate volume.

**SAMPLE  
ANALYSIS:**

**Refer to FSFL SOP-529: Maintenance and Operation of Flow Injection  
Analyzer QuikChem 8000**

**CALCULATIONS:**

Calibration is performed by injecting standards. The data system will then prepare a calibration curve by plotting response versus standard concentration. Sample concentration is calculated from the regression equation.

Report only those values that fall between the lowest and highest calibration standards. Samples exceeding the highest standard should be diluted and reanalyzed.

Report results in % P<sub>2</sub>O<sub>5</sub> as APA in fertilizer.

**APPROVAL:**

Approved by: \_\_\_\_\_ *Patricia A. Lucas* \_\_\_\_\_ Date: 07/15/09

**Signature**

**Bureau Chief**

\_\_\_\_\_  
**Title**

**METHOD REVISION HISTORY:**

---

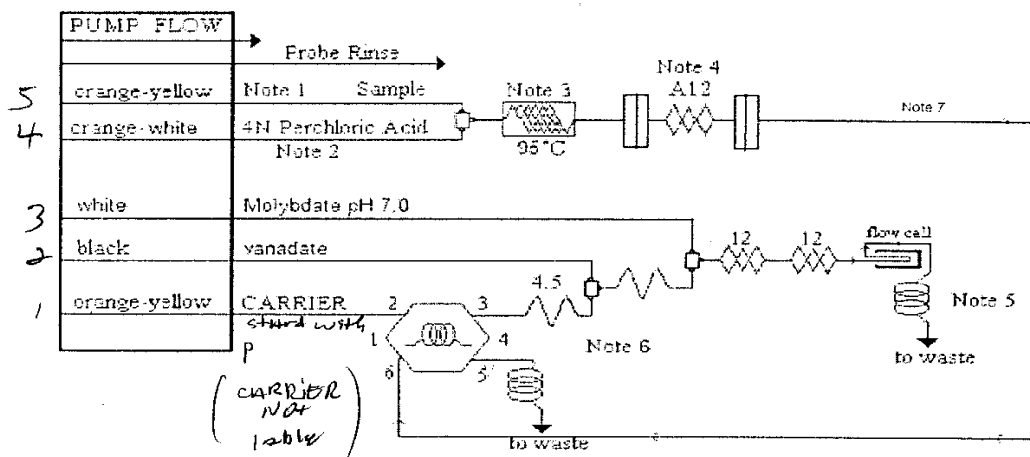
<b>Version</b>	<b>Date</b>	<b>Description</b>	<b>Author</b>
Original	02/10/94	Replaces P-100.00	W. M. Bell
Original	08/22/02	Replaces FM-501	W. M. Bell
Revised	07/15/09	Replaces FM-540	Ethel Thuotte

**REFERENCE:**

1. AOAC 15th Edition, Method 963.03B, 978.01
2. QuikChem Method 15-115-01-3-B


PHOSPHATE SYSTEM SCHEMATIC

11.3. PHOSPHORUS MANIFOLD DIAGRAM



**Carrier:** Reagent 4 (2.5 N HClO<sub>4</sub>)  
**Manifold Tubing:** 0.8 mm (0.032 in) i.d. This is 5.2 μL/cm.  
**QC8000 Sample Loop:** 13 cm of 0.8mm i.d. tubing  
**Interference Filter:** 420 nm

**Apparatus:** An injection valve, a heater, a 10 mm path length flow cell, and a colorimetric detector module are required.

The  denotes 1500 cm of tubing at the temperature shown  
**4.5:** 70 cm of tubing on a 4.5 cm coil support  
**12:** 255 cm of tubing on a 12 cm alternating coil support

- Note 1:** This is the sample line. It is connected to the autosampler probe. The orange-yellow pump tube is cut 3 cm outside of the tabs on each side. The other end of the orange-yellow pump tube is connected to the tee (with 4 N Perchloric Acid), which goes into the heater. If the samples are to be analyzed for more than one analyte, the sample line can be split using a Tee. (See diagram on the following page).
- Note 2:** 50 cm of 0.032" tubing is used to connect the perchloric acid line to the tee.
- Note 3:** 1500 cm of tubing wrapped on the heater
- Note 4:** Aluminum alternating coil with heat sinks. 255cm of 0.032" tubing is wrapped on this coil
- Note 5:** 50 cm of 0.022" i.d. tubing backpressure loop
- Note 6:** 50 cm of 0.022" i.d. tubing backpressure loop
- Note 7:** 60 cm of 0.03" i.d. tubing is used to connect the outlet of the cooling coil to port 6 of the valve.
- Note 8:** Steel pins must be removed from the PTA's and transmission lines. Use PN 50015A, acid resistant small nipples to connect transmission lines to the pump tubes.
- Note 9:** PVC PUMP TUBES MUST BE USED WITH THIS METHOD